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14. ABSTRACT This research aims to develop and optimize a novel and environmentally benign supercritical fluid (SCF)-assisted melt compounding process for mass producing lightweight, high-performance polymer-nanocellulose composites with desired optical (e.g. transparency) and mechanical properties. This study resulted in several useful advances and developments including (1) a better understanding of nanofibrillated cellulose nanocomposite behavior; (2) Knowledge of the plausible mechanisms of dispersing nanofibers through the incorporation of SCF; (3) the					
15. SUBJECT TERMS Nanocomposite, Supercritical Fluid Assisted Process					
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Report Title

A NOVEL SUPERCRITICAL FLUID-ASSISTED FABRICATION TECHNIQUE FOR PRODUCING TRANSPARENT NANOCOMPOSITES

ABSTRACT

This research aims to develop and optimize a novel and environmentally benign supercritical fluid (SCF)-assisted melt compounding process for mass producing lightweight, high-performance polymer-nanocellulose composites with desired optical (e.g. transparency) and mechanical properties. This study resulted in several useful advances and developments including (1) a better understanding of nanofibrillated cellulose nanocomposite behavior; (2) Knowledge of the plausible mechanisms of dispersing nanofibers through the incorporation of SCF; (3) the processing know-how and guidelines for nanocomposites; (4) the viable formulation of novel solid and microcellular polymer nanocomposites; and (5) novel application areas for and benefits of the resultant materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received

Paper

TOTAL:

Number of Manuscripts:

Books

Received

Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Srikanth Pilla	0.50
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FTE Equivalent: 0.50

Total Number: 1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
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Lih-Sheng Turng	0.00	
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FTE Equivalent: 0.00

Total Number: 1

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
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Kerry Aschenbach	0.50	Mechanical Engineering
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FTE Equivalent: 0.50

Total Number: 1

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Three types of studies were conducted:

1. Transparent nanocomposites based on poly(methyl methacrylate) (PMMA) and cellulose nanocrystals (CNC) nanocomposites
2. Transparent green polymer blends based on polylactic acid (PLA) and polypropylene carbonate (PPC)
3. Transparent green nanocomposites based on polylactic acid (PLA), polypropylene carbonate (PPC) and nanofibrillated cellulose (NFC)

Technology Transfer

STIR PROJECT TITLE:
A NOVEL SUPERCRITICAL FLUID-ASSISTED FABRICATION
TECHNIQUE FOR PRODUCING TRANSPARENT NANOCOMPOSITES

Final Progress Report

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&
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List of Appendixes, Illustrations and Tables

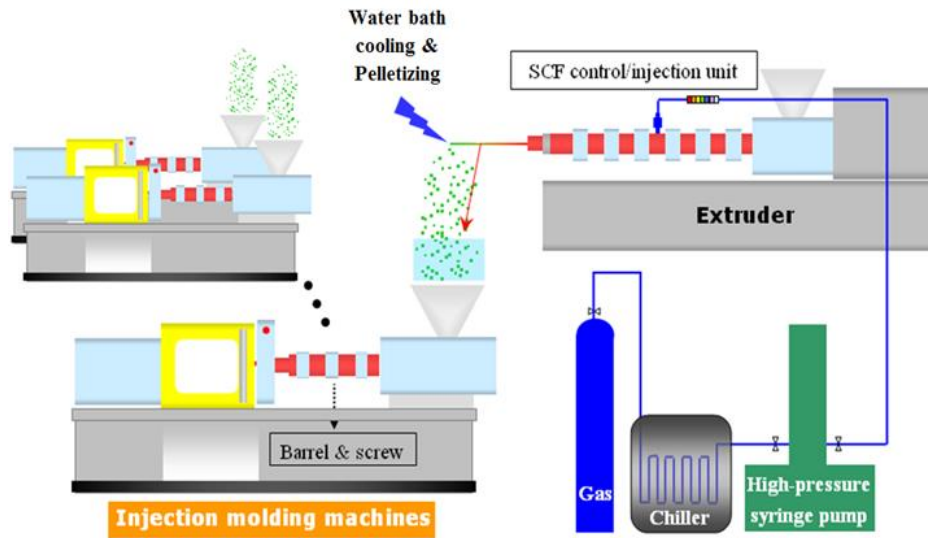


Fig-1: Schematic of SIFT Technology



Fig-2: Optical Transparency of Neat PMMA and PMMA-1%CNC Nanocomposite

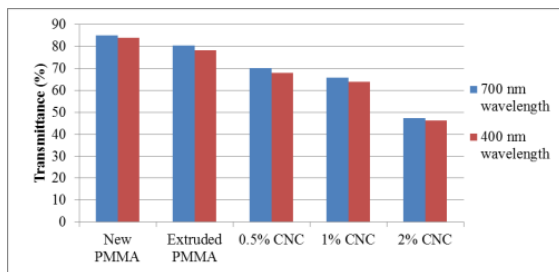


Fig-3: Optical Transparency at 400 and 700nm Wavelengths

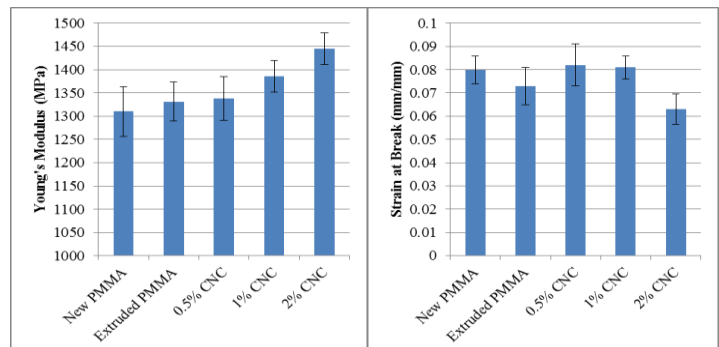


Fig-4: Tensile Moduli and Strain-at-break of PMMA and PMMA-CNC Nanocomposites

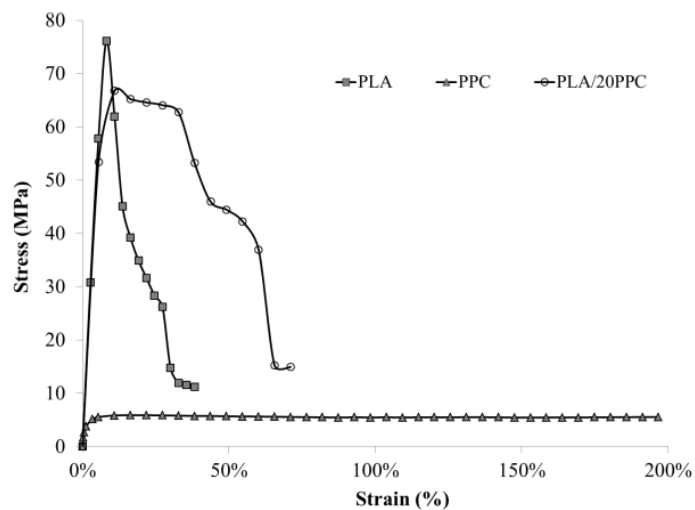


Fig-5: Tensile Stress-Strain Curves of PLA, PPC and Their Blend

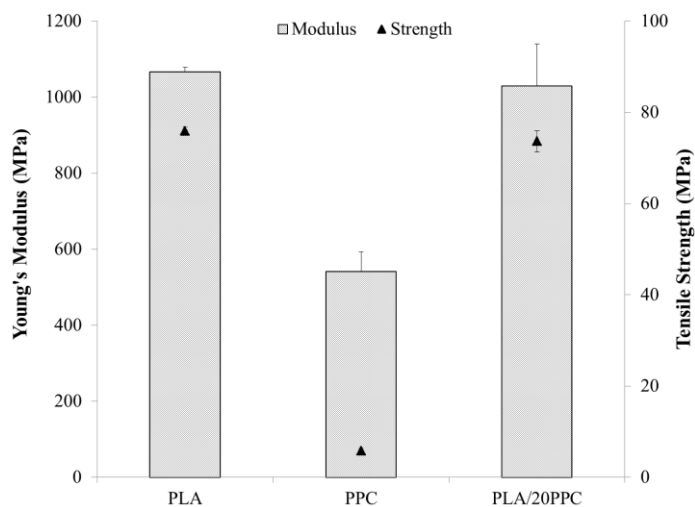


Fig-6: Tensile Moduli and Strengths of PLA, PPC and Their Blend

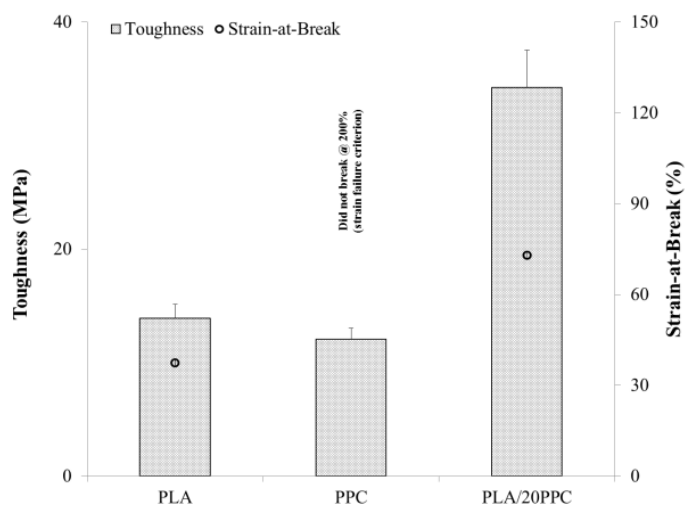
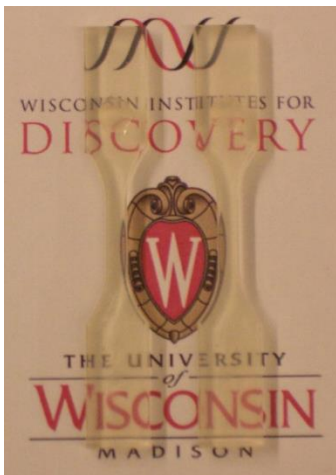
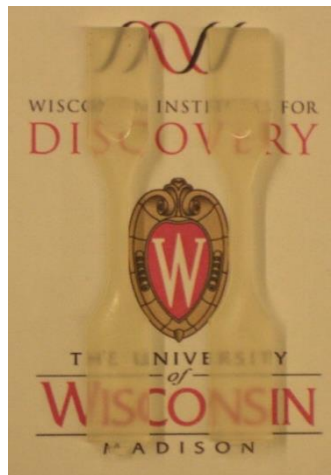


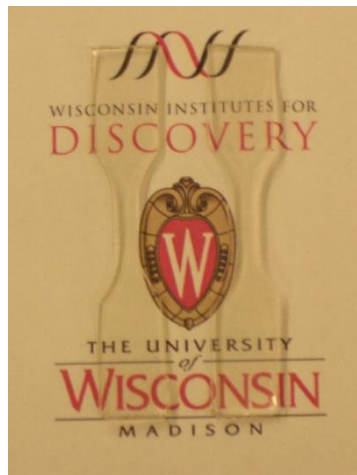
Fig-7: Toughness and Strain-at-break of PLA, PPC and Their Blend



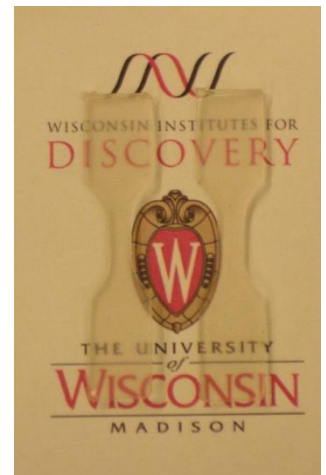
Pure PLA



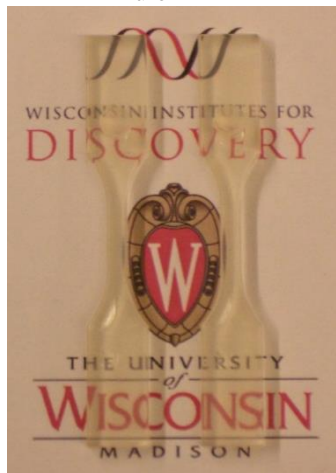
PLA-1%CNC



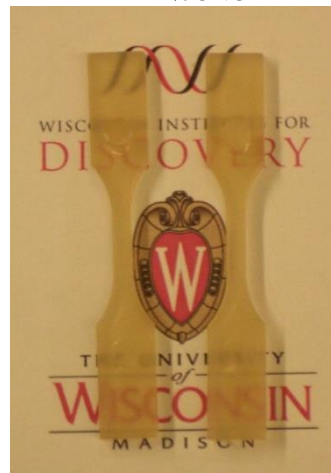
Pure PPC



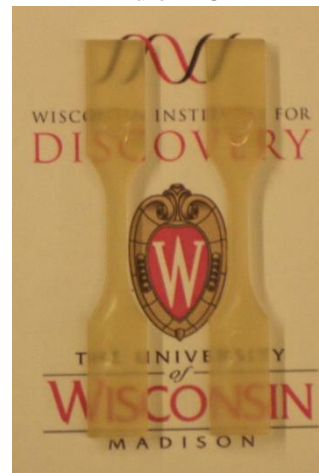
PPC-1%CNC



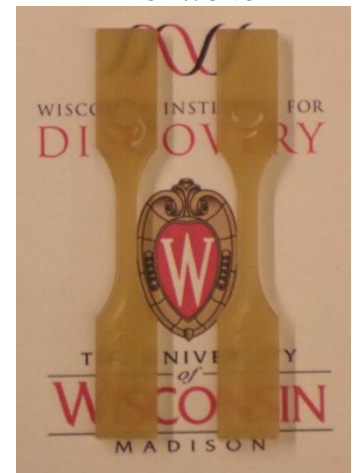
PLA+PPC



PLA-PPC-0.5%CNC



PLA-PPC-1%CNC



PLA-PPC-2%CNC

Fig-8: Optical Transparency of PLA-PPC-CNC Nanocomposites

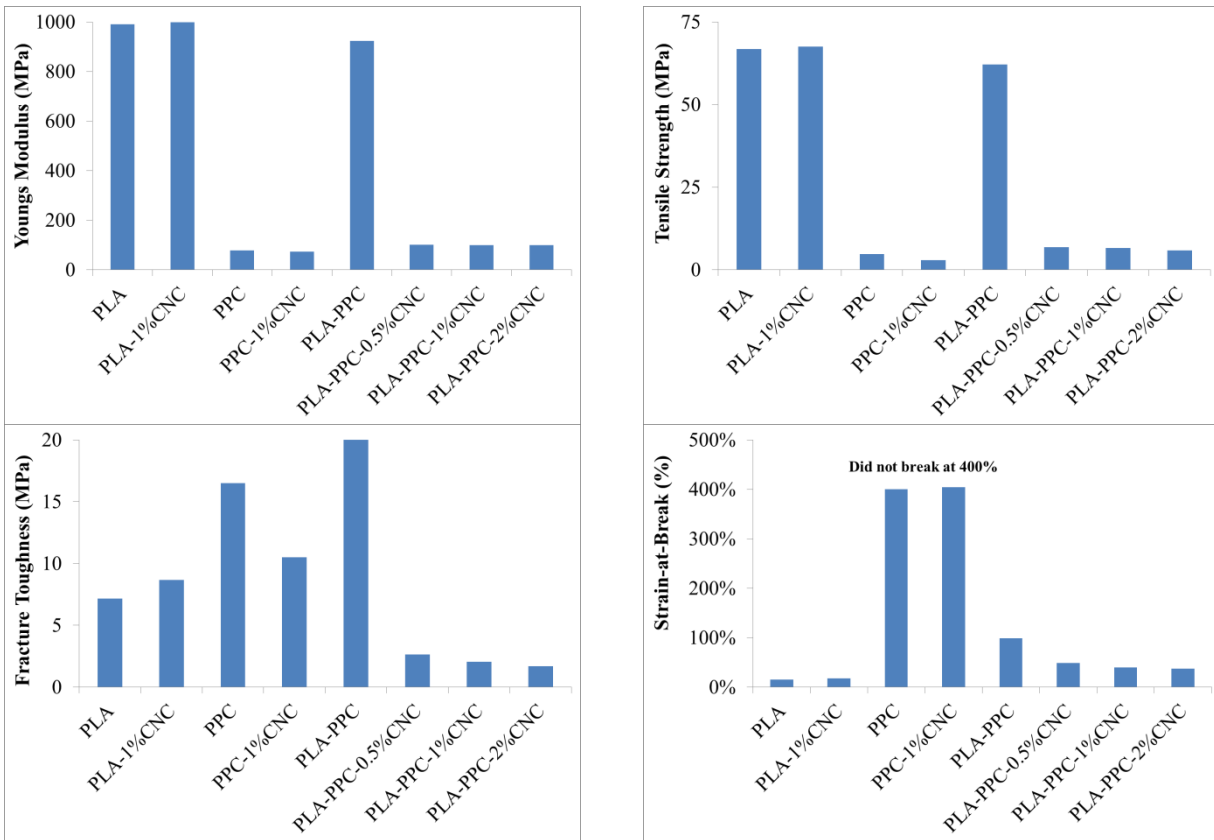


Fig-9: Mechanical Properties of PLA-PPC-CNC Nanocomposites

Table-1: Process Conditions:

Extrusion	
Feed rate	21 gram/min
Screw Speed	100 RPM
CO2 Content	1.6%
Temperature (from feed zone to die)	140/145/155/150/150/150/150/155 deg. C
Injection Molding	
Injection flow rate	70 cm ³ /sec
Packing	1500 bar for 2 sec
Screw recovery speed	15 m/min
Back pressure	100 bar
Temperature (from feed zone to die)	145/150/155/165/160 deg. C

Statement of Problem Studied

Project Objectives:

This research aims to develop and optimize a novel and environmentally benign supercritical fluid (SCF)-assisted melt compounding process for mass producing lightweight, high-performance polymer-nanocellulose composites with desired optical (e.g. transparency) and mechanical properties. In addition, this study could result in several useful advances and developments including (1) a better understanding of nanofibrillated cellulose nanocomposite behavior; (2) knowledge of the plausible mechanisms of dispersing nanofibers through the incorporation of SCF; (3) the processing know-how and guidelines for nanocomposites; (4) the viable formulation of novel solid and microcellular polymer nanocomposites; and (5) novel application areas for and benefits of the resultant materials. The transparent nanostructured materials developed in this study can be applied for variety of Army applications such as in visors, windshield, canopies, etc. Finally, the continuous process being developed in this study would lead to a low-cost route for fabrication of nanocellulose-based polymer nanocomposites.

Research Highlights:

Three types of studies were conducted:

1. Transparent nanocomposites based on poly(methyl methacrylate) (PMMA) and cellulose nanocrystals (CNC) nanocomposites
2. Transparent green polymer blends based on polylactic acid (PLA) and polypropylene carbonate (PPC)
3. Transparent green nanocomposites based on polylactic acid (PLA), polypropylene carbonate (PPC), and nanofibrillated cellulose (NFC)

Study-1: PMMA-CNC Nanocomposites

PMMA is a transparent thermoplastic polymer with a minimum processing temperature of 185°C. CNCs are highly crystalline nanostructures which undergo thermal degradation at temperatures above 165°C. Thus, it is difficult to fabricate PMMA-CNC nanocomposites without thermally degrading the nano-fillers using conventional polymer processing techniques. Henceforth, this study proposes to use a unique supercritical fluid assisted fabrication technology wherein the supercritical fluid such as carbon dioxide, plasticizes the polymer melt thereby allowing us to process the materials at significantly lower temperatures.

In this study, a novel Supercritical fluid laden pellets Injection molding Foaming Technology (SIFT) invented by the PI and his co-workers was used. In this process, the blowing agent is injected and incorporated into the polymer during an extrusion process using a high-pressure syringe pump connected to the extruder barrel. The extruded polymer-gas solution was immediately cooled and pelletized, such that the pellets still contain gas and foaming capability. Then the gas-laden pellets can be used in conventional injection molding machines to produce foamed parts. A schematic of this approach is shown in Fig-1.

Experiments

Material

- PMMA: Evonik Acrylite M30
- Freeze dried CNC powder provided by Forest Products Laboratory (FPL), added at 0.5, 1 and 2 wt% content.

Equipment

- Extruder: Leistritz ZSE 18 HPe twin-screw extruder equipped with a Isco 260D syringe pump
- Injection molding machine: Arburg Allrounder 320S

Process Temperature: 185°C

Summary of Most Important Results

Optical Transparency:

Neat PMMA and PMMA-NFC nanocomposites were tested for optical transparency. Fig-2 shows the optical transparency of neat PMMA and PMMA-1%CNC nanocomposite. The quantified transmittance values as measured by UV-Vis at 400 and 700 nm wavelengths were shown in Fig-3. As shown in the figure, PMMA showed the highest transmittance i.e. 85% and 83% while PMMA-2%CNC showed the lowest i.e. 48% and 46% at 700 and 400 nm, respectively.

Mechanical Properties:

Fig-4 shows the tensile modulus and strain-at-break of PMMA and PMMA-CNC nanocomposites. As can be observed from the figure the addition of CNC enhanced the tensile moduli of the PMMA-CNC nanocomposites. This is because adding fillers to a polymer restrains the movement of its chains, thereby increasing the stiffness. On the other hand, a consistent strain-at-break was observed with the addition of CNC except for PMMA-2%CNC nanocomposite. For 2%CNC nanocomposite, the reduction in strain-at-break is likely due to decreased deformability because of the restriction offered by the CNC. Hence, it can be inferred that the optimum content of CNC to achieve consistent deformability as that of pure PMMA is <2%.

Future Work

- Optimize the gas content to lower the processing temperature further.
- Investigate higher CNC content and find an optimized range for obtaining superior mechanical and optical properties.

Study-2: PLA-PPC Transparent Binary Blends

The aim of this study is to develop environment-friendly transparent polymer blends. Polymer blends and composites offer feasible solutions to tailor material properties for targeted applications. In this study, PLA and PPC binary blends have been investigated to obtain a balanced portfolio of properties which have the potential to leverage their use in sustainable applications. Both PLA and PPC are highly transparent and have competing properties that will leverage synergistic effects and thereby result in high-strength blends.

PLA is synthesized from corn-based sugars via ring-opening polymerization. PPC is synthesized from carbon dioxide and epoxide in the presence of a metal catalyst. In addition to being naturally derived, PLA and PPC are compostable under simulated conditions in a composting facility.

Experiments

Material

- PLA: 8052D from Nature Works
- PPC: QPAC-40 from Empower Materials

Equipment

- K-mixer for dry material blending
- DSM-Xplore micro-injection molding machine

Process Temperature: 180°C

Summary of Most Important Results

Mechanical Properties:

Static tensile properties were tested using an Instron Universal Testing Machine (Model #5967). Fig-5 shows the stress-strain curves of PLA, PPC, and their blend. The test termination criterion was set to be either the specimen break point or 200%, whichever occurred first. The crosshead rate was set at 1.25 mm/min.

All specimens were observed to exhibit varying degrees of ductility. The addition of PPC induced considerable cold drawing, which was due to the ductile nature of PPC.

Fig-6 shows the tensile modulus and strength of the pure polymers and their blend. Among the polymers, PLA and PPC possessed the highest and lowest stiffness and strength, respectively. PLA/PPC blend showed comparable strength to that of PLA. Though no compatibilizers were added to the blend, the synergistic effect between the dispersed phase PPC and continuous phase PLA enhanced the modulus and strength such that the overall properties of the blend were comparable and consistent with that of the PLA matrix.

Fig-7 shows the strain-at-break and toughness of PLA, PPC, and their binary blend. The toughness was computed by integrating the area under the stress-strain curve. As can be observed from the figure, among all the materials, PLA-PPC blend possessed the highest toughness and PLA and PPC had comparable toughness. Also, PPC did not break at 200% (test termination criterion). However, PLA and PLA-PPC blend have strain-at-break values of 37% and 73%, respectively. Thus, it can be inferred that compared to polymers, the synergistic effect of the blends showed superior mechanical properties.

Future Work

- Investigate SIFT fabrication technology on PLA-PPC polymer blends

Study-3: PLA-PPC-CNC Transparent Nanocomposites

In this study, PLA-PPC-CNC transparent nanocomposites were investigated. CNC is prepared by acid hydrolysis and consist primarily of crystalline cellulose.

Experiments

Material

- PLA: 8052D from Nature Works
- PPC: QPAC-40 from Empower Materials
- CNC: Supplied by Forest Products Lab, USDA

Equipment

- Leistritz ZSE 18 extruder for material compounding
- Boy micro-injection molding machine

Process Temperature: 180°C

Processing

The materials, i.e. PLA, PPC and CNC, were compounded using the Leistritz ZSE 18 twin-screw extruder. Pure polymers were also extruded so as to maintain the same thermal history. All the materials were then injection molded using a Boy micro-injection molding machine.

Summary of Most Important Results

Transparency:

Fig-8 shows the optical transparency of fabricated nanocomposites. As shown in the figure, pure polymers show the highest optical transparency. The PLA-PPC blend showed a transparency comparable to that of pure PLA possibly indicating that the blends are immiscible [Ning, et al.]. The addition of 1% CNC to PLA and PPC decreased the transparency slightly, possibly due to some agglomeration. Similarly, the addition of CNC to PLA-PPC blend decreased the transparency which might be due to agglomeration. In addition, some thermal degradation was observed, possibly due to CNC which is susceptible to moisture absorption as well as sensitive to temperature. Thus, the higher the CNC content, the more evident is the thermal degradation.

Mechanical Properties:

Static tensile properties were tested using an Instron Universal Testing Machine (Model #5967). Fig-9 shows the Young's modulus, tensile strength, fracture toughness, strain-at-break of the PLA-PPC-CNC nanocomposites. As shown in the figure, for pure PLA and PPC, the addition of 1% CNC did not affect the Young's modulus. However, for the polymer blend, i.e. PLA-PPC, the addition of CNC has resulted in substantial decrease in modulus. Thus, it could be inferred that the processing method employed as well as the materials design, collectively resulted in better dispersion of CNCs in pure polymers as opposed to blended ones. Similar results were observed for tensile strength and strain-at-break. Also, the pure PPC and PPC-1%CNC samples didn't break even at 400% strain. Hence, the tests were stopped at 400% in order to protect the equipment which has a limitation in test bed. The fracture toughness was computed as the area under the stress-strain curve. As can be seen, the PLA-PPC blend exhibited superior toughness than that of pure polymers. This shows the miscibility of the blend which is beneficial in increasing the toughness. However, the addition of CNC to the blend has substantially reduced the toughness indicating agglomeration of CNC.

Future Work

- Investigate SIFT fabrication technology on PLA-PPC-CNC nanocomposites, which not only helps to process these materials at reduced temperatures thereby alleviating thermal degradation but also assists in better dispersion of CNC.

Bibliography

- Ning, W., Xingxiang, Z., Jiugao, Y., Jianming, F., "Partially miscible poly(lactic acid)-blend-poly(propylene carbonate) filled with carbon black as conductive polymer composite", Polymer International, Vol. 57, pp. 1027–1035 (2008)